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(54) TITLE: COMPOSITE WATER-SWELLABLE ELASTOMERS AND METHOD OF PREPARATION THEREOF

### (57) Abstract

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DESCRIPTIONComposite water swellable elastomers and method of  
5 preparation thereofTechnical Field

The invention relates to composite water swellable elastomers and method of preparation thereof.

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Background Art

It is known that the plasticized polyvinyl chloride (PVC) or synthetic butadiene-acrylonitrile rubber may be filled with powdered hydrogels, as ion exchangers, or 15 crosslinked poly(2-hydroxyethylmethacrylate) in production of thin-walled articles e.g. artificial leathers. The reason for the hydrogel filler use was to incorporate an ability of water vapor transport through the material, see for example US Patents No. 3,875.261 and No. 3,928.704 (V. Heidingsfeld 20 et al) and US Patent No. 4,228.205 (S. Hudeček et al). These materials are useful for shoes, gloves, upholstery and parts of clothing but did not find any application in the medical field.

Surface wettable silicone elastomers have been prepared 25 in the past by grafting of hydrophilic monomers on the surface or in the elastomers bulk as is described in "Radiation grafted hydrogels on silicon rubber as new biomaterials" in the book "Biomedical Applications of Polymers", by B. D. Ratner and A. S. Hoffman. The grafting 30 was successfully performed only with the mixture of N-vinylpyrrolidone and 2-hydroxyethylmethacrylate.

It has been previously found that silicone elastomers filled with powdered hydrophilic polymer fillers according the US Patent No. 4,696.974 (J. Šulc et al) have very suitable properties for applications as biomaterials. This 5 hydrophilic composite material contains powdered hydrophilic filler in the crosslinked silicone polymer which forms a continuous matrix of the composite. The final material and the object made of the material is prepared by thoroughly mixing the filler with non-vulcanized silicone rubber and 10 vulcanizing agent which is followed by press-molding or injection-molding of the desired article.

As at the point of the processing of the above described material in the liquid phase only the silicone elastomer is present and during the vulcanization of the article the 15 silicone elastomer "floats" on the surface and the homogenous hydrophobic layer of silicone rubber without the hydrophilic filler - the "skin" is formed on the surface of the article.

This hydrophobic layer changes dramatically the transport characteristics of the material, surface 20 wettability and prevents the material's use for certain applications such as drug delivery, hydrophilic catheters, defined transport of water and water vapors, etc.. The further disadvantage is that the materials having only small amounts of the hydrophilic filler (0.1 - 10 %) cannot be 25 prepared the way that the filler is homogeneously distributed through the whole entire bulk.

These characteristics are very important for materials which are intended for the directed liberation of small amounts of water-soluble low molecular weight compounds e.g. 30 drugs. As well as the small amounts, the way, how the material described in the US Patent No. 4,696.974 is

prepared, does not allow the incorporation of the extremely large amounts of the hydrophilic filler because such an overloaded silicone elastomer loses its ability to flow and is not processable. The kind of fillers which can be used for 5 the material described in the US Patent No. 4,696.974 is limited as the degradable and thermically unstable fillers cannot be used for example for high temperature vulcanizing silicone elastomer systems, the reactive groups containing fillers cannot be used in RTV silanol or vinyl vulcanizing 10 systems due to their interference with the vulcanization systems.

Now it has been found that the disadvantages of composite materials received by mixing the powdered filler and the silicone rubber can be overcome by new composite 15 materials consisting of an elastomeric matrix and an "in-situ" generated hydrophilic filler. The "in-situ" technique of hydrophilic filler incorporation produces non-agglomerated fine particles uniformly distributed through-out the elastomeric matrix up to the very surface and provides an 20 elastomer with two integrated continuous phases. These materials have an improved continuous communication of the hydrophilic phase with higher diffusivity of water and water-soluble compounds.

25 Disclosure of the Invention

Object of the invention are composite water swellable elastomers consisting of a hydrophobic elastomeric component and a hydrophilic polymeric component in which the hydrophobic as well as the hydrophilic component are forming 30 a continuous or communicating matrix.

Another object of the composite water swellable elastomers according to the invention is that the hydrophobic elastomeric component is selected from the group consisting of filled and unfilled, vulcanized and not-vulcanized 5 silicone rubber, natural rubber, synthetic butadiene-styrene rubber, butadiene rubber, isoprene rubber, isobutylene-isopropylene rubber, ethylene-propylene rubber, brombutyl rubber, chloroprene rubber, butadien-acrylonitrile rubber, acrylate rubber, urethane rubber, fluorocarbon rubber, 10 chlorosulphonated polyethylene rubber, chlorinated polyethylene rubber, ethylene vinyl acetate rubber, polysulfide rubber and hydrine rubber.

As hydrophilic polymeric component according to the invention there are used polymers based on hydrophilic 15 monomers selected from the group consisting of glycol monomethacrylates and acrylates, dihydroxyester-monomethacrylates or acrylates, acrylamide, methacrylamide, N-substituted and N,N-disubstituted acryl or methacrylamides, methacrylic and acrylic acids, N-vinylpyrrolidon and their 20 combinations.

The method of preparation of the composite water swellable elastomers according to the present invention consists in that inside the matrix of the hydrophobic elastomeric component and/or filler the precipitation or 25 solution polymerization of a hydrophilic monomer or monomer mixture in the presence of one or more solvents, a crosslinking agent and an initiator of radical polymerization is performed.

The process of the invention is performed in such a way 30 that the hydrophobic elastomeric component is prior to the polymerization swollen with the mixture of one or more

monomers, one or more solvents, crosslinking agent and initiator of radical polymerization or said hydrophobic elastomeric component is mixed with said mixture, and after completion of the polymerization the solvent is removed by 5 evaporation, distillation, extraction or washing.

The crosslinking agent containing at least two polymerizable unsaturated bonds being according to the invention selected from the group consisting of ethylene glycol dimethacrylate or diacrylate, di- and tri-ethylene 10 dimethacrylate and diacrylate, 1,3-propanediol dimethacrylate and diacrylate, divinyl benzene, sorbitol dimethacrylate, bis-acrylamide, allyl methacrylate.

In the general the crosslinking monomer can be present at a level of from about 0.01 to about 10 weight percent, and 15 preferably from about 0.5 to about 3 weight percent of the total weight of the monomer-solvent mixture.

As initiators of radical polymerization there are used initiators selected from the group consisting of azocompounds as azo-bis(isobutyronitrile), 2,2'-azo-bis(2,4-dimethyl- 20 pentanenitril), peroxycarbonates as isopropylpercarbonate, peroxyesters, peroxyethers, the redox initiation systems consisting of peroxy sulfates-methabisulfates, peroxy sulfates-TEMED and UV initiators such as benzoinethers.

As solvent which is a solvent for the monomer and 25 swelling agent or solvent for the hydrophobic phase there are used solvents selected from the group consisting of water, aliphatic alcohols, glycols, cyclic ethers, cellosolves, dimethyl sulfoxide, dimethyl formamide, diacetone, aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons and the 30 mixtures thereof.

In a further embodiment the present invention relates to a method of preparation of the composite water swellable elastomers according to the present invention comprising the precipitation polymerization or solution polymerization being 5 repeated one or more times using the same or different monomers, solvents, crosslinking agents and initiators.

In an additional embodiment the present invention relates to a method of preparation of the composite water swellable elastomers comprising the precipitation or solution 10 polymerization being performed only in the swollen surface layer.

A further aspect of the present invention relates to a method of preparation of the composite water swellable elastomers comprising the precipitation polymerization or 15 solution polymerization being performed either only in the hydrophobic matrix or only in the hydrophilic filler.

In a further embodiment the present invention relates to a method of preparation of the composite water swellable elastomers according to the present invention comprising the precipitation polymerization or solution polymerization being 20 performed in the hydrophobic matrix and the hydrophilic filler.

The continuous or communicating matrix according to the invention represents a compact polymer or particles, which 25 are contiguous to each other. In case of the communicating matrix the particles of the hydrogel being separated from the hydrophobic phase due to the surface interaction are contacting each other and enable the mutual communication between each other such as the swelling with water.

30 The composite water swellable elastomers according to the present invention contain the hydrogel particles, which

had been incorporated into the hydrophobic matrix and/or into the filler by the precipitation or solution polymerization, uniformly distributed in the whole volume.

The hydrogel particles can be formed "in-situ" in the 5 vulcanized rubber as well as in the non-crosslinked polymer, which after the completion of precipitation polymerization and the removal of the used solvents is additionally vulcanized.

The method of generating the hydrophilic filler "in- 10 situ" has when compared with the method of preparation according to the US Patent No. 4,696.974 the advantage in that the formed filler is uniformly distributed and has a micron or sub-micron size without the necessity of intensive grinding or mixing. At the same time it abolishes the 15 possibility of agglomeration of filler particles and problems with the incompatibility of hydrophilic particles having a great surface with the hydrophobic polymer. By this method it is also possible to prepare a filler covalently bound to the non-vulcanized elastomer.

20 According to the present invention the elastomer can be swollen with a mixture of one or more monomers and one or more solvents containing a suitable initiator of radical polymerization and eventually a crosslinking agent.

The other possibility in accordance with the present 25 invention is the admixing of the said mixture of monomers and solvents into the non-vulcanized rubber.

The choice of the initiators is affected by the solubility in the used monomers or solvents.

The solvent or the mixture of solvents is being chosen 30 according to the intention to which phases or to which of the

two phases has the hydrogel to be incorporated to: the hydrophobic matrix, the hydrophilic filler, the hydrophobic filler and the hydrophobic matrix, and the hydrophilic filler, but always such a kind of a solvent which can after 5 the precipitation polymerization is completed be removed by evaporation, distillation, extraction or washing.

The amount of the incorporated hydrogel in the elastomer or rubber bulk depends on the elastomer's or rubber's ability to swell in the solvent, on the concentration of monomer or 10 monomers in the mixture solvent-monomer. In case of non-crosslinked rubber it depends on the miscibility and processability (workability) of the filled rubber. The size of the particles formed in the precipitation polymerization depends on the monomer concentration, the kind of solvent and 15 the diffusivity of the monomer through the elastomer matrix and the swellability of the solvent. The particle size is in the range of from 0.001 to 1.0 micron.

The advantage of this method is in that a very small amount of hydrogel particles 0.1 - 10.0 % wt can be 20 incorporated into the elastomeric matrix while the sub-micron particles having a large interphase surface still maintain homogenous dispersion and communication between each other. On the other hand it is possible to prepare the materials with extremely high content of the hydrogel particles by a 25 repeated precipitation polymerization. The materials prepared according to the present invention have the same hydrogel particles content in the bulk as well as at the surface. These materials can be advantageously utilized for a directed transport of water-soluble low molecular weight compounds.

30 The method according to the invention allows to introduce the hydrogels into the final products made of

vulcanized elastomers produced by the well known techniques as extrusion, injection molding, press-molding: tubings, catheters, films, etc.. If only the surface of the article is desired to be hydrophilized only the surface of the article 5 can be swollen in the solvent-monomer mixture prior to the polymerization which creates a gradient of hydrophilicity. This method of additional filling of elastomers can be useful for example for the catheters and the products which should not change their dimensions due to the treatment. The 10 precipitation polymerization can be repeated several times while the same or different monomers and solvents are being used.

This way the blend of hydrophilic polymers, precipitated particles inside the polymeric filler forming a filler with 15 interpenetrating network, eventually covalently bound, copolymers which would be otherwise hard to prepare due to their unfavorable copolymerization parameters, can be introduced to the elastomer and different levels of hydration, wettability, transport of water soluble compounds 20 and mechanical properties can be reached.

The elastomers having different hydrogel particles next to each other and/or hydrogel particles in a form of precipitated polymer inside the hydrophilic filler can be easily prepared as well. By the precipitation polymerization 25 of reactive monomers (glycidyl methacrylate, methacryloylchloride etc.) it is possible to prepare the hydrophilic fillers which have an ability to react further, covalently bound, graft another specially biologically active entities (heparin, enzymes, proteins, amino acids etc.). 30 Membranes made of these invented materials have optimal characteristics for an oxygen transport between two aqueous

environments as they have a large interphase surface inside the material, between the hydrophilic filler and the hydrophobic matrix, and are usable for the oxygenators etc.

The monomers or monomer mixtures can be chosen for 5 instance so that after completion of the precipitation polymerization, the removal of solvents and the swelling of the thus received hydrophilic silicone elastomer with water, there is being formed a water swellable filled and optical transparent silicone rubber suitable for instance for the 10 preparation of contact or intraocular lenses or other medical means, where the transparency is an inevitable condition.

Another advantage of the invented method comparing with for example the mixing of the hydrophilic filler with non-vulcanized silicone high temperature vulcanizing rubber is 15 that the filler, which would otherwise undergo undesirable changes by the heating during the vulcanization, can be incorporated to the already vulcanized rubber overcoming that way the exposure to the high temperature.

When preparing the filler by solution polymerization, 20 the monomer or the mixture of monomers can be chosen so as to form a water-soluble polymer, which serves as a continuously released lubricant with advantage in applications as are catheters.

25 Examples

Example 1

The filled silicone elastomer tubing was being swollen in a mixture of 30 % wt of 2-hydroxyethylmethacrylate (HEMA) 30 containing 1.5 % wt ethylene glycol dimethacrylate (EGDMA) and 70 % wt of toluene containing 0.5 % wt azo-

bis(isobutyronitrile) (ABIN) as a thermoinitiator to an equilibrium which was achieved in 2 hours. After this period of time the monomer-solvent mixture content in the tubing was 70 % wt. The tubing was then placed to the jar purged with 5 nitrogen saturated with toluene vapors having a temperature of 80°C. After 1 hour the precipitation polymerization of the HEMA inside the silicone tubing was completed, the tubing was removed from the jar and toluene dried out in the vacuum oven at 60°C, 10mm/Hg for 2 hours. This way treated silicone 10 tubing had a water content 12 % wt and a wettable surface.

#### Example 2

The silicone tubing filled with poly(2-hydroxyethyl methacrylate) (PHEMA) prepared according to example 1 was 15 swelled in a water solution of 10 % wt of sodium methacrylate, 10 % wt of 2-hydroxyethyl methacrylate (HEMA) containing 2 % wt ethylene glycol dimethacrylate (EGDMA) and 1% wt ammonium persulfate as a water-soluble thermoinitiator, for 2 hours when the equilibrium swelling was achieved. Then 20 the tubing was placed to the reactor filled with the inert nitrogen atmosphere saturated with a water vapor and heated to 80°C. After 1 hour the tubing was removed and placed to the beaker with distilled water. The water content was 53 % wt and the surface of the tubing was wettable and slippery.

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#### Example 3

The sheet of the composite material made according the US Patent 4,696.974 containing 50 % of powdered poly(2-hydroxyethyl methacrylate) (PHEMA) filler having a water 30 content of 20 % wt and a non-wettable surface has been swollen until the equilibrium was reached in the mixture of

30 % wt 2-hydroxyethyl methacrylate(HEMA) containing 1.5 % wt ethylene glycol dimethacrylate (EGDMA) and 70 % wt toluene containing 1 % azo-bis(isobutyronitrile) (ABIN). Then the reaction mixture monomer-solvent with the immersed tubing was 5 purged with nitrogen and heated up to 60°C for 1,5 hour in the jar immersed in the water bath. After the polymerization completion the sheet was taken out of the reactor and dried at 65°C, 10 mm/Hg for 2 hours in vacuum oven. The sheet of the composite material treated this way had 32 % wt water and 10 had a wettable surface.

#### Example 4

The silicone elastomer tubing having an outer diameter of 5 mm has being pulled through the mixture of 15 % wt of 15 HEMA containing 2 % wt EGDMA, 15 % wt methacrylic acid and 70 % wt toluene containing 1.5 % wt ABIN as an initiator. The mixture was purged with nitrogen. The immersion time of the tubing in the mixture in the immersion zone was 3 min. After passing through the immersion zone the tubing was pulled 20 through the polymerization zone which was filled with nitrogen saturated with toluene vapor and heated to 80°C. The exposure time was 15 min. Then the tubing was dried in the vacuum oven as in example 3, conditioned in 2 % aqueous solution of ammonium hydroxide and washed in distilled water. 25 The surface of the tubing was highly wettable, slippery and the diameter of the tubing increased not more than 0.2 mm.

#### Example 5

The sheet having the thickness of 1 mm prepared from a 30 two component transparent non-filled silicone elastomer vulcanized by vinylic addition was placed in a vessel

containing the monomer mixture of 20% wt of dimethylaminoethyl methacrylate, 10% wt methacrylic acid, 3% wt ethylene glycol methacrylate, 66,5% wt toluene and 0,5% wt 2,2'-azo-bis(2,4-dimethylpentanenitril) as initiator of 5 thermal radical polymerization. The sheet was left in the mixture for 2 hours at room temperature for swelling through uniformly. Afterwards the mixture was purged with nitrogen for 3 minutes and the vessel was immersed in a water bath with the temperature of 60° C. After 2 hours the sheet was 10 taken out of the reaction vessel and the toluene removed in the vacuum oven as in example 3. After equilibrium swelling in distilled water the sheet became transparent, wettable, with a content of water of 30% wt and significantly better 15 mechanical properties in comparison with the starting non-filled silicone elastomer.

#### Example 6

A mixture consisting of 25 g 2-hydroxyethyl methacrylate, 5 g methacrylic acid, 0.5 g ethylene glycol 20 dimethacrylate, 1.0 g t-butylperoxyneodekanoate, 69.5 g of silicone elastomer and 150 g toluene was poured into a 500 ml reaction flask and purged with nitrogen. The flask was closed and fixed into a rotation evaporator and immersed in the water bath with a temperature of 50°C. The mixture was left 25 in the flask under slow rotation for 6 hours till the completion of the precipitation polymerization. Then a reflux condenser was connected to the flask and the toluene was together with the non-reacted rests of the monomers removed by evaporation under rotation at 50°C and vacuum of 10 mm/Hg. 30 The thus received filled non-crosslinked silicone elastomer containing 28.5 % wt of the hydrophilic and uniformly

distributed hydrogel filler of sub-micron size was used for the preparation of the sheet.

Example 7

5        The silicone elastomer tubing treated according to example 1 was swollen to the equilibrium state in a mixture containing 30% wt N-vinylpyrrolidon, 0.3% wt t-butyl-peroxy-2-ethylhexanoate and 69.7% wt toluene. Afterwards the polymerization and the treatment were performed in the same 10 way as in example 3. The obtained tubing had after wetting with water a slippery surface.

Claims

1. Composite water swellable elastomers consisting of a hydrophobic elastomeric component and hydrophilic polymeric component in which the hydrophobic as well as the hydrophilic component are forming a continuous or communicating matrix.  
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2. Composite water swellable elastomers according to claim 1, characterized in that the hydrophobic elastomeric component is selected from the group consisting of a filled or unfilled, vulcanized or non-vulcanized silicone, natural rubber, synthetic butadiene-styrene rubber, butadiene rubber, isoprene rubber, isobutylene-isoprene rubber, ethylene-propylene rubber, ethylene-propylene rubber, chlorobutyl rubber, bromobutyl rubber, chloroprene rubber, butadiene-acrylonitrile rubber, acrylate rubber, urethane rubber, fluorocarbon rubber, chlorosulfonated rubber, polyethylene rubber, chlorinated polyethylene rubber, ethylene vinyl acetate rubber, polysulphide rubber, hydrine rubber.  
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3. Composite water swellable elastomers according to claim 1 and 2 characterized in that the hydrophilic polymeric component is being formed by a polymer based on the hydrophilic monomers being selected from the group consisting of glycol mono-methacrylates and acrylates, dihydroxyester mono-methacrylates, acrylamide, methacrylamide, N-substituted acrylamide and methacrylamide, N,N-substituted acrylamide and methacrylamide, methacrylic and acrylic acids, N-vinylpyrrolidon and their  
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combinations.

4. Method of preparation of the composite water swellable elastomers of claims 1 to 3, characterized in that inside the matrix of the hydrophobic elastomeric component and/or the filler the precipitation or solution polymerization of a hydrophilic monomer or monomer mixture in the presence of one or more solvents, a crosslinking agent and an initiator of the radical polymerization is performed.
5. Method according to claim 4, characterized in that the hydrophobic elastomeric component is swollen in the mixture of one or more monomers, one or more solvents, a crosslinking agent and an initiator of the radical polymerization or said hydrophobic component is mixed with the said mixture, and after the polymerization is completed the solvent is removed by evaporation, distillation, extraction or washing.
10. Method according to claims 4 ad 5, characterized in that the crosslinking agent containing at least two polymerizable unsaturated bonds is selected from the group consisting of ethylene glycol dimethacrylate or diacrylate, di- and tri-ethyleneglycol dimethacrylate and diacrylate, 1,3-propanediol dimethacrylate and diacrylate, divinyl benzene, sorbitol-dimethacrylate, bis-acrylamide, allylmethacrylate.
20. Method according to claims 4 to 6 characterized in that the amount of the crosslinking monomer is in the range of from 0.01 to 10 % wt of the total weight of the monomer-
25. Method according to claims 4 to 6 characterized in that the amount of the crosslinking monomer is in the range of from 0.01 to 10 % wt of the total weight of the monomer-
30. Method according to claims 4 to 6 characterized in that the amount of the crosslinking monomer is in the range of from 0.01 to 10 % wt of the total weight of the monomer-

solvent mixture.

8. Method according to claims 4 to 7 characterized in that the amount of the crosslinking monomer is the range of 5 from 0.5 to 3 % wt of the total weight of the monomer-solvent mixture.
9. Method according to claims 4 to 8 characterized in that the initiator of radical polymerization is selected from the group consisting of azocompounds as azo-10 bis(isobutyronitrile), 2,2'-azo-bis(2,4-dimethylpentanenitril), peroxycarbonates as isopropylpercarbonate, peroxyesters, peroxyethers, redox initiation systems consisting of peroxy sulfates-methabisulfates, peroxy sulfates-TEMED and UV initiators as benzoinethers.
- 15 10. Method according to claims 4 to 9 characterized in that the solvent which is a solvent for the monomer and a swelling agent or solvent for the hydrophobic phase is selected from the group consisting of water, aliphatic 20 alcohols, cyclic ethers, glycols, cellosolves, dimethylsulphoxide, dimethylformamide, diacetone, aromatic and aliphatic hydrocarbons, chlorinated hydrocarbons and the mixture thereof.
- 25 11. Method of preparation of water swellable elastomers of claims 1 to 3, characterized in that the process of precipitation or solution polymerization is repeated one or more times using the same or different monomers, solvents, crosslinking agents and initiators of the 30 radical polymerization.

12. Method of preparation of water swellable elastomers of claims 1 to 3, characterized in that the precipitation or solution polymerization is performed only in the swollen 5 surface layer.

13. Method of preparation of water swellable elastomers of claims 1 to 3, characterized in that the precipitation or solution polymerization is performed only in the 10 hydrophobic matrix.

14. Method of preparation of water swellable elastomers of claims 1 to 3, characterized in that the precipitation or solution polymerization is performed only in the 15 hydrophilic filler.

15. Method of preparation of water swellable elastomers of claims 1 to 3, characterized in that the precipitation or solution polymerization is performed in the hydrophobic 20 matrix and the hydrophilic filler.

# INTERNATIONAL SEARCH REPORT

International Application No  
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**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 C08F283/12 C08F291/02

According to International Patent Classification(IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 569 964 A (LEE DO I ET AL) 11 February 1986 see claim 1 ---	1-3
X	EP 0 643 083 A (ESSILOR INT) 15 March 1995 see claims 1,9-14 ---	1-10
X	US 4 196 065 A (GAUSSSENS GILBERT ET AL) 1 April 1980 see claim 1 ---	1-10
X	US 4 696 974 A (SULC JIRI ET AL) 29 September 1987 cited in the application see claim 1 ---	1-3
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

national Application No

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

national Application No

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